Relation of Adhesion Tension to "Liquid Absorption"

A DISSERTATION

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN THE UNIVERSITY OF MICHIGAN

By

O. H. Greager

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Relation of Adhesion Tension to "Liquid Absorption"

Liquid absorption values (Gardner-Coleman method) have been determined for three powdered solids with a series of different liquids. Adhesion tension values were either available or were obtained for each system. Both sets of data were obtained with identical materials.

A simple linear relationship has been found to exist between liquid absorption and adhesion tension for all those systems in which the liquid forms a zero angle of contact against the solid. The liquid absorption is the least for those liquids which show the highest adhesion tension against the solid.

For those systems in which the liquid forms a finite contact angle against the solid the liquid absorption is lower than would be expected from the foregoing relationship. The larger the angle of contact (and the less the adhesion tension) the less the oil absorption.

THE determination of the so-called "oil absorption" values of pigments has become a common practice in the paint and color varnish industry. A knowledge of these values serves as an aid in regulating the character of the finished product.

At present it appears to be generally conceded that "oil absorption" values are, for the most part, dependent on three factors: (1) the specific surface of the solid material, which

is governed chiefly by the fineness of the pigment powder; (2) the degree of wetting of the solid by the liquid phase; and (3) the method used in making oil absorption measurements. It has been shown (*2*) that the degree of wetting of a solid by a liquid can be determined by means of adhesion tension data and can be expressed in terms of absolute units. It follows, then, that a definite relationship should exist between "liquid absorption," to use the more general term, and adhesion tension.

A definite attempt to correlate "liquid absorption" and adhesion tension was first made by Baldwin (*1*). He made use of the limited data then existing in the literature (*2*, *3*, *4*) for the adhesion tensions of various liquids against carbon and silica. From these data, together with his own values for the liquid absorptions obtained with similar liquids and supposedly similar solids, an equation was formulated to express the interrelation of liquid absorption, specific surface, and adhesion tension. The adhesion tension data available to him, however, were rather limited for a critical treatment. Moreover, it has recently been shown that carbon blacks from different sources show quite different adhesion tension values against given liquids (*5*). In the light of additional data it is felt that, although Baldwin's views are in general correct, the conclusions drawn from his work are somewhat in error and the equation presented by him is not justified.

Experimental

The data presented in this paper were obtained with the three solids silica, carbon black, and calcium fluoride. The determinations of the liquid absorption values for the first two solids were made with materials identical with those used by Bartell and Osterhof in their work on adhesion tension. In addition, use was made of their more complete data, which unfortunately are as yet unpublished. Calcium fluoride was used, not because it has any interest as a pigment, but because fairly complete adhesion tension data for this solid had recently been obtained by the writers.

The determination of liquid absorption was carried out according to the method of Gardner and Coleman (*6*), as follows: Twenty grams of powder are placed in a beaker and the liquid added slowly from a buret. As the liquid comes in contact with the powder, the particles thus made wet cling together and form a small ball of paste. Further additions of liquid are directed onto this ball, and the surrounding dry powder is lifted from the outer edges and placed over it. Finally, all the powder will be incorporated in the large lump of paste. Up to this point, the mass will not smear the walls of the glass container; in other words, the wetting property toward an external phase is absent. The addition of one or two drops at this point, however, will cause the mass to soften and smear the glass. This is the end point of the determination. The liquid absorption factor is then ex-

pressed as the volume of liquid (in cc.) required to saturate 100 grams of material.

The data for the three solids (Table I) lead to conclusions somewhat different from those presented by Baldwin.

When the liquid absorption values are plotted against the adhesion tension values, the curves shown in Figures 1, 2, and 3 are obtained. A linear relationship between liquid absorption and adhesion tension appears to exist for liquids which wet the solid with a zero angle of contact. It will be noted, however, that all liquids which form finite angles of contact against the solid show considerable deviation from this linearity. Furthermore, in the case of calcium fluoride, for which the values for three liquids which form finite contact

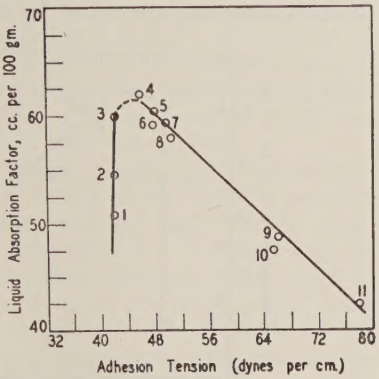


Figure 1—Calcium Fluoride

Table I—Adhesion Tension *vs.* Liquid Absorption

	No.[a]	Liquid	Contact Angle	Adhesion Tension	Liquid Absorption
			Degrees		
Calcium fluoride (Figure 1)	1	Methylene iodide	32.50	42.3	51.0
	2	Tribromohydrin	16.25	43.0	54.5
	3	α-Bromonaphthalene	12.50	43.0	60.0
	4	Bromobenzene	0	46.1	62.0
	5	Chloroform	0	48.5	59.0
	6	Toluene	0	48.5	60.5
	7	Benzene	0	50.1	59.5
	8	Bromoform	0	50.7	58.0
	9	Ethyl carbonate	0	65.9	48.8
	10	Butyl acetate	0	65.2	47.5
	11	Water	0	76.5	42.5
Silica (Figure 2)	1	α-Bromonaphthalene	19.90	41.9	58.0
	2	Benzene	0	52.4	65.5
	3	Toluene	0	54.7	66.0
	4	Chloroform	0	60.0	63.5
	5	Butyl acetate	0	73.5	61.0
	6	Ethyl carbonate	0	74.3	59.5
	7	Isobutyl alcohol	0	81.1	58.0
	8	Water	0	82.8	58.5
Carbon black (Figure 3)	1	Water	40.60	54.7	382
	2	Isobutyl alcohol	0	56.6	436
	3	Ethyl carbonate	0	65.6	416
	4	Butyl acetate	0	65.8	424
	5	Decalin	0	76.4	400
	6	Tetralin	0	76.7	396
	7	Benzene	0	81.1	392
	8	Toluene	0	82.1	330
	9	α-Bromonaphthalene	0	89.2	370

[a] Numbers agree with numbers used in Figures 1, 2, and 3.

angles have been determined, the extent of the deviation increases as the angle of contact increases.

This irregular behavior on the part of liquids which form finite angles of contact against the solid and also the scarcity of published data on adhesion tension referred to were un-

doubtedly the cause of Baldwin's erroneous interpretation of his results. In his work the logarithms of the adhesion tension values were plotted against the logarithms of the liquid absorption values. This brought the points for the liquids which form finite angles of contact into line, but the points representing the values for some of the other liquids

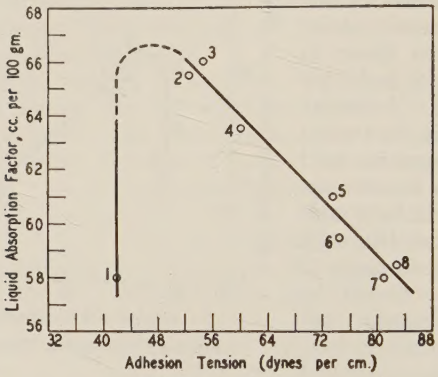


Figure 2—Silica

fell away from this line. He assumed the deviation in these cases to be due to experimental errors.

The results obtained in the present work indicate that a simple linear relationship exists between adhesion tension and liquid absorption for those liquids which form a zero angle of contact against the solid. The deviation from this relationship in the case of the other liquids is neither accidental nor

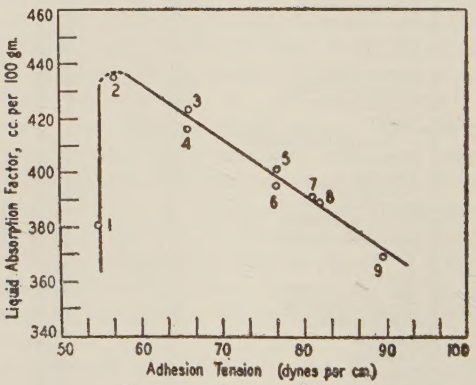


Figure 3—Carbon Black

the result of the presence of impurities and may, we believe, be logically explained as follows.

Let us first consider the case of two liquids between parallel plates and in contact with the plane surface of the lower plate. Consider that one liquid (*A*) will wet the surface with a zero angle of contact, while the other (*B*) forms with it a

definite equilibrium contact angle. A drop of liquid A, when placed on this surface, will spread indefinitely, or until at least a monomolecular layer has been formed. A drop of liquid B, however, will spread on this same surface only until a configuration of the drop which corresponds to the equilibrium contact angle for this system has been reached. In other words, if several drops of liquid A were placed on this surface they would all coalesce in time, but several drops of liquid B might be arranged in such a manner that, on spreading out until the equilibrium contact angle was reached, no two drops would meet and coalesce.

Next there may be considered the amounts of these two liquids that it would be necessary to add before a point of contact would be established with the upper parallel plate. In the case of liquid A, which spreads with a zero angle of contact, the addition of successive amounts would result in the formation of uniform layers of increasing height, until finally contact would be established with all points on the plate at once. The volume of liquid that had been added up to this point would be equal to the product of the area of the bounded surface and the distance between the plates. In carrying out the same test with liquid B, however, contact

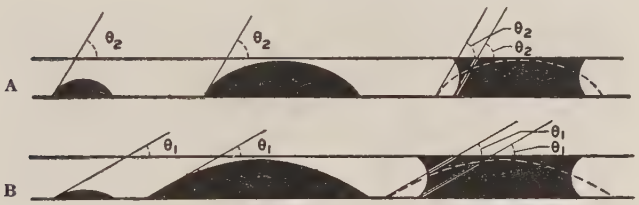


Figure 4—Angle of Contact for Liquids A and B

could be established with the upper plate before a volume corresponding to that for liquid A had been added. That is, individual drops could reach the necessary height without having spread out to such an extent that they would coalesce with other drops. A considerable portion of the volume between the plates would, in such a case, be occupied by air.

The larger the angle of contact, the greater will be the amount of air entrapped, and consequently the greater will be the deviation from the normal relationship. This will be seen from Figure 4, which represents two liquids of different contact angle, θ, between the parallel plates. As the drops become larger, contact is finally established with the upper surface. The equilibrium angle, θ, for a given liquid must always be the same (disregarding gravitational effects), regardless of the size of the drop. Thus, the larger the angle, the less liquid will be required to establish contact with the upper surface. This is the case for the liquid shown in Figure 4, A which has an angle of contact greater than the liquid shown in Figure 4, B.

When dealing with the particles of a powder, the case is

but little different. It is probable that air is never completely displaced from the powder (in the Gardner-Coleman method) with liquids which form finite contact angles. Assuming spherical particles, the void or pocket between these particles would appear as shown in Figure 5. When liquid is introduced between these particles, the liquid-air

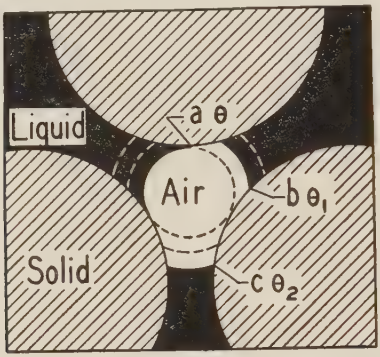
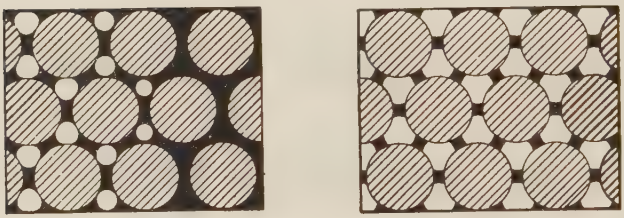


Figure 5—Volume of Air Entrapped Is Dependent upon Contact Angle



a *b*

Figure 6—Amount of Liquid Absorbed Is Dependent upon Contact Angle

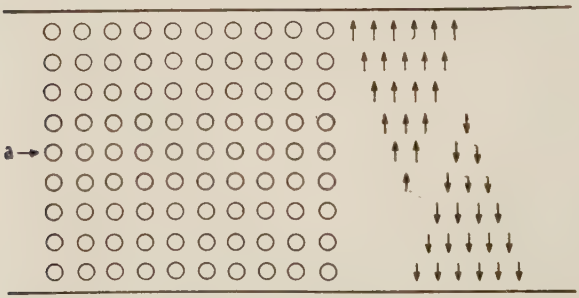


Figure 7—Attractive Force Operative through Liquid Layer between Solid Phases

interface takes up a position according to the angle of contact. If the angle be zero, the interface will advance as far as possible toward the pocket, and the air bubble if entrapped will tend to be spherical. This position is indicated as *a* in Figure 5. If a finite contact angle is formed against the

solid by the liquid, the interface can advance only to the position where the configuration of the solid particles forces it to meet the solid with the equilibrium contact angle. For a liquid of small angle of contact, the interface would take up the position at *b;* if the angle is larger, the interface would be at *c*. Thus, as for the above case of two parallel surfaces, the greater the angle of contact the greater the amount of air entrapped, and accordingly a lesser amount of liquid would be held within the powder. This is shown in Figure 6, in which *a* represents a clump of solid particles wet with a liquid of small or zero contact angle. The various interfaces are well out toward the pockets, and wide bands of liquid are held in the powder. With a liquid of larger angle of contact (*b*), the interfaces are further removed from the pocket, and the bands of liquid held in the powder are narrower.

From Figures 1, 2, and 3 it is apparent that the amount of liquid with zero contact angle absorbed by a powder de-

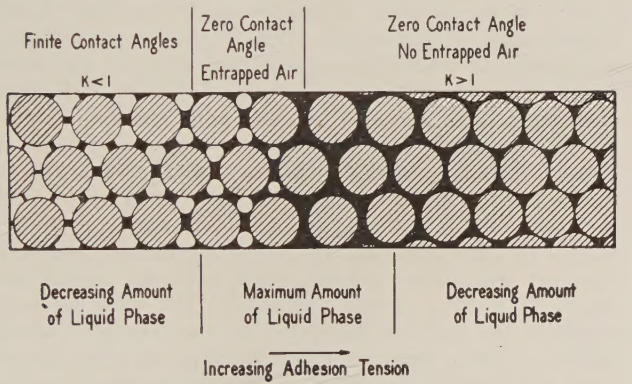


Figure 8—Amount of Liquid Absorbed Is Dependent upon Adhesion Tension and Contact Angle

creases in proportion to the adhesion tension solid-liquid. Without attempting a critical treatment of this relationship, it may be tentatively explained as follows:

In a 2-phase solid-liquid system, the solid exerts a certain attractive force on the liquid. Regardless of the precise nature of the attraction gradient from the solid-liquid interface into the liquid, a preponderance of evidence indicates that the influence is operative over many molecular layers. This is shown diagrammatically in Figure 7. The liquid between two particles in a paste, as represented by liquid molecules (*a*), might thus be attracted by both solid surfaces. With a limited amount of liquid, the tendency will be to draw the particles closer together, and the stronger the attraction (or the higher the adhesion tension) the greater will be this tendency. It follows that the closer together the particles the smaller would be the amount of liquid which could be held in the paste. In other words, the greater the

adhesion tension of the liquid against the solid, the less will be the volume of liquid that will be required to "wet" the powder. This relationship was actually found in the experimental work.

In view of the foregoing discussions, it becomes evident that the amount of oil held by the powder may depend to quite an extent upon the precise method employed in bringing together the oil and the powder. Greatest variations are to be expected with liquids giving a large angle of contact with the solid. With such liquids much entrapped air may be held.

It is believed that a fairly exact representation of the condition which may exist within a system of a powder wet by different liquids is given in Figure 8. Here the particles of powder are represented as spheres. The relation of volume of liquid to volume of entrapped air is shown by the black and white portions, respectively. At the left is represented a liquid having a large angle of contact, resulting in relatively small volume of liquid and large volume of air. The central portion of the diagram represents conditions when a zero contact angle is approached. With liquids which wet more completely, air would be displaced from the solid and would tend to escape from the mass. A liquid giving a high degree of wetting (high adhesion tension) would tend to displace the air completely. As the adhesion tension is further increased, the solid particles are drawn closer together, with the result that the relative amount of liquid held by the solid becomes less. If the above-expressed views are correct, it follows that the maximum of "liquid absorption" should be obtained with those liquids which give an intermediate degree of wetting against the solid. The most favorable condition for high oil absorption by the Gardner-Coleman method would be obtained with a liquid giving a zero contact angle with the solid, but having a low adhesion tension against the solid.

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